

METHODS AND COMPOSITIONS FOR TREATING  
SUBTERRANEAN FORMATIONS USING  
HIGH IONIC STRENGTH GELLING AGENT POLYMERS

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

[0001] The present invention relates to methods, aqueous treating fluid compositions and high ionic strength gelling agent polymers for treating subterranean formations.

2. DESCRIPTION OF THE PRIOR ART.

[0002] Viscous treating fluids are used in a variety of operations and treatments in oil and gas wells. Such operations and treatments include forming gravel packs in well bores, fracturing producing zones, performing permeability control treatments and the like.

[0003] Hydrocarbon producing wells are often stimulated by hydraulic fracturing treatments. In hydraulic fracturing, a viscous fracturing fluid, which also functions as a carrier fluid, is pumped into a subterranean zone to be fractured at a rate and pressure such that one or more fractures are formed in the zone. Proppant particles, e.g., graded sand, for propping the fractures open are suspended in the fracturing fluid and are deposited in the fractures when the fracturing fluid viscosity is reduced. The fracturing fluid viscosity is reduced by including a delayed viscosity breaker in the fracturing fluid that causes it to revert to a thin fluid. The proppant particles deposited in the fractures function to prevent the fractures from closing so that conductive channels are formed through which produced hydrocarbons can readily flow.

[0004] Aqueous fracturing fluids are generally viscosified by mixing a hydratable polysaccharide gelling agent polymer with water. For example, guar gum and its derivatives are

often used to viscosify aqueous fracturing fluids. Guar gum is a random coil polymer that can be readily crosslinked with various cross-linking agents, e.g., metal ions. Once crosslinked, guar and guar derivatives can form highly viscoelastic gels that approach near zero suspended particle settling rates.

**[0005]** It is desirable to increase the effectiveness of gelling agent polymers in general, and this has been achieved in the prior art to a significant degree by grafting ionic groups, for example carboxyl groups, onto the gelling agent polymer chain. Since like charges tend to repel each other, the carboxyl groups force the flexible coiled polymer to become more linear. Maximizing the linearity results in an enlarged radius of gyration, which in turn results in a lesser amount of gelling agent being required to generate a gelled treating fluid.

**[0006]** A problem is that the viscosity increasing effect of carboxyl groups is greatly reduced as the pH of the fluid drops below 7. This is due to the fact that the carboxylate ions are salts of weak acids and tend to hydrolyze. In addition, the solubility of anionic groups in water containing multivalent metal ions such as calcium and magnesium is small making gelling agent polymers containing anionic groups, e.g., carboxyl groups, less soluble in hard water. Thus, anionic groups render gelling agent polymers sensitive to ionic strength whereby the viscosity of the polymer in a salt solution is much less than the viscosity in fresh water. The salt sensitivity is undesirable since the aqueous liquids used in well treating fluids often contain chloride salts to inhibit swelling of formation clays or are formed with brines or seawater.

**[0007]** Thus, there are needs for improved methods of treating subterranean formations with viscous aqueous treating fluids, gelling agent polymers having decreased sensitivity to low pH and hard water, and improved gelling agent polymers having high ionic strength.

## SUMMARY OF THE INVENTION

[0008] By the present invention, methods of treating subterranean formations with viscous aqueous treating fluids, improved viscous aqueous treating fluids and improved gelling agent polymers are provided which meet the needs described above and overcome the deficiencies of the prior art. The methods of treating subterranean formations penetrated by well bores basically comprise the following steps. A viscous aqueous treating fluid composition is prepared or provided comprising water and a high ionic strength gelling agent polymer. Thereafter, the viscous aqueous treating fluid composition is introduced into the subterranean formation.

[0009] The viscous aqueous treating fluid compositions of this invention comprise water and a high ionic strength gelling agent polymer. The high ionic strength gelling agent polymer is a sulfonated polymer that provides improved rheological properties to the treating fluid, as do conventional carboxylated gelling agent polymers. However, unlike carboxylated gelling agent polymers, the sulfonated gelling agent polymer maintains improved viscosity properties at pH's below 7 and in hard water.

[0010] The improved high ionic strength gelling agent polymers of this invention are sulfonated gelling agent polymers.

[0011] The objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of preferred embodiments which follows.

## DESCRIPTION OF PREFERRED EMBODIMENTS

[0012] The methods of this invention for treating subterranean formations penetrated by well bores basically comprise the following steps. A viscous aqueous treating fluid composition

is prepared or provided comprising water and a high ionic strength sulfonated gelling agent polymer. The viscous aqueous treating fluid composition is then pumped into a well bore to treat the subterranean formation.

[0013] The viscous aqueous treating fluids of this invention are comprised of water and a sulfonated gelling agent polymer.

[0014] The water utilized in the viscous aqueous treating fluid compositions of this invention can be fresh water or salt water. The term "salt water" is used herein to mean unsaturated salt water including brines and seawater.

[0015] The high ionic strength sulfonated gelling agent polymers that can be utilized in accordance with the present invention include, but are not limited to: sulfonated biopolymers such as xanthan and succinoglycon; sulfonated synthetic polymers such as sulfonated polyvinyl alcohols, sulfonated polyacrylamides, sulfonated polyacrylates; sulfonated acrylamide/acrylic acid copolymers; sulfonated polysaccharides; and sulfonated polysaccharide derivatives. Sulfonated polysaccharides include, but are not limited to, sulfonated galactomannan gums such as guar gum, gum arabic, gum ghatti, gum karaya, tamarind gum, locust bean gum and the like, and sulfonated cellulose derivatives. Examples of preferred sulfonated galactomannan gum gelling agent polymers are sulfonated guar, sulfonated hydroxypropylguar, sulfonated carboxymethylhydroxyethyl guar and sulfonated carboxymethylguar. Examples of preferred sulfonated cellulose derivatives are sulfonated carboxymethylcellulose, sulfonated carboxymethylhydroxyethylcellulose, sulfonated hydroxyethylcellulose, sulfonated methylhydroxypropylcellulose, sulfonated methylcellulose, sulfonated ethylcellulose, sulfonated propylcellulose, sulfonated ethylcarboxymethylcellulose, sulfonated methylethylcellulose, and

sulfonated hydroxypropylmethylcellulose. Of the sulfonated gelling agent polymers, sulfonated guar is the most preferred.

[0016] The sulfonated gelling agent polymer utilized is preferably present in the aqueous treating fluid in an amount in the range of from about 20 lbs to about 60 lbs of polymer per 1000 gal of the aqueous treating fluid, and more preferably from about 30 lbs to about 45 lbs per 1000 gal. The preparation of sulfonated polymers is generally well known by those skilled in the art.

[0017] A crosslinking agent can optionally be added to further enhance the viscosity of the aqueous treating fluid. Examples of suitable crosslinking agents that can be utilized include, but are not limited to, boron compounds such as boric acid, disodium octaborate tetrahydrate, sodium diborate and pentaborates, ulexite and colemanite, compounds that can supply zirconium IV ions such as zirconium lactate, zirconium lactate triethanolamine, zirconium carbonate, zirconium acetylacetonate and zirconium diisopropylamine lactate, compounds that can supply titanium IV ions such as titanium ammonium lactate, titanium triethanolamine and titanium acetylacetonate, aluminum compounds such as aluminum lactate and aluminum citrate, and compounds that can supply antimony ions. Of these, boric acid is the most preferred.

[0018] When used, the crosslinking agent is included in the aqueous treating fluid in an amount in the range of from about 2 lbs to about 40 lbs per 1000 gal of the aqueous treating fluid, and more preferably from about 4 lbs to about 12 lbs per 1000 gal.

[0019] The methods of this invention for fracturing subterranean formations and the fracturing fluids utilized are improved due to the decreased sensitivity of the high ionic strength sulfonated gelling agent polymer to low pH and hard water. The methods basically comprise the following steps. A viscous aqueous fracturing fluid composition is prepared or provided comprising water and a high ionic strength sulfonated gelling agent polymer. The water can be

fresh water or hard water, i.e., salt water including brines and seawater. The viscous aqueous fracturing fluid can optionally also include a cross-linking agent to increase its viscosity. The viscous aqueous fracturing fluid is then introduced into the subterranean formation at a rate and pressure sufficient to form one or more fractures therein.

**[0020]** A preferred method of this invention for treating a subterranean formation penetrated by a well bore comprises the steps of: (a) preparing or providing a viscous aqueous treating fluid composition comprising water and a high ionic strength sulfonated gelling agent polymer; and (b) introducing the viscous aqueous treating fluid composition into the subterranean formation.

**[0021]** A preferred method of this invention for forming one or more fractures in a subterranean zone penetrated by a well bore comprises the steps of: (a) preparing or providing an aqueous fracturing fluid composition comprising water and a high ionic strength sulfonated gelling agent polymer; and (b) introducing the aqueous fracturing fluid composition into the subterranean zone at a rate and pressure sufficient to form one or more fractures therein.

**[0022]** A preferred viscous aqueous treating fluid composition of this invention comprises water and high ionic strength sulfonated gelling agent polymer.

**[0023]** A preferred high ionic strength sulfonated gelling agent polymer of this invention is selected from the group consisting of sulfonated gelling agent biopolymers, sulfonated synthetic gelling agent polymers, sulfonated polysaccharide gelling agent polymers and sulfonated polysaccharide derivative gelling agent polymers.

**[0024]** In order to further illustrate the methods and compositions of the present invention, the following examples are given.

### Example 1

[0025] To demonstrate the stability of sulfonated gelling agent polymers to potassium chloride, the viscosity of a 0.5% solution of sulfonated guar polymer was compared to that of a 0.5% solution of carboxymethyl guar at 75°F. Viscosity measurements were made with increasing additions of potassium chloride.

[0026] The results are shown in Table 1 below. The viscosity of carboxymethyl guar decreases significantly with initial additions of potassium chloride. The sulfonated polymer basically maintains its viscosity.

**Table 1. Viscosity After KCl Addition**

%KCl	Viscosity, cP	
	CMG*	SULF*
0	26.34	28.7
0.25	20.29	---
0.5	20.15	---
1	19.08	27.3
2	18.75	26.3
3	18.82	25.5
4	18.69	24.8
5	18.49	24.2
6	18.19	23.6
7	18.14	23.2
8	17.89	22.9
9	17.68	22.3
10	17.65	22.2
11	17.90	22.5
12	17.61	22.6

\*CMG = Carboxymethyl guar

\*SULF = Sulfonated guar

### Example 2

[0027] To demonstrate the superior stability of sulfonated gelling agent polymers in the presence of divalent cations, a 0.5% solution of sulfonated guar polymer was compared to that of a 0.5% solution of carboxymethyl guar. Viscosity measurements were made at 75°F with increasing additions of calcium chloride.

[0028] The results are shown in Table 2 below. The viscosity of carboxymethyl guar decreases significantly with initial additions of calcium chloride. The sulfonated polymer basically maintains its viscosity.

**Table 2. Viscosity After CaCl<sub>2</sub> Addition**

%CaCl <sub>2</sub>	Viscosity, cP	
	CMG*	SULF*
0	24.4	28.9
0.125	19.9	28.7
0.25	19.5	28.9
0.50	19.8	28.9
0.75	--	28.9
1.0	20.6	28.9
2.0	21.7	28.9
3.0	22.2	29.1
4.0	22.7	29.1
5.0	23	29.0
6.0	23	29.1
10	26	30.6

\*CMG = Carboxymethyl guar

\*SULF = Sulfonated guar

### Example 3